Fluctuation Relations of Phase Transitions - Externally Driven Crystallization

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Core Junior Project (FNR Luxembourg)
Theory of Soft Condensed Matter
University of Luxembourg
Three Parts

• **I**: Compressing the system into the solid phase
• **II**: Periodically compressing/decompressing across the coexistence pressure
• **III**: Studying active particles
Three Parts

• I : Driving the system away from an equilibrium state
• II : Driving the system in a non equilibrium steady state
• III : Driving the system away from a non equilibrium steady state
Main Research Goal

• Study the dissipation in colloidal systems
• Connect structures to dissipation locally
• Advance the formalism of phase transition and fluctuation relations
• Bridge the two fields of research
Main Idea

• Work is defined, i.e. dissipated energy can be calculated.

• Study macroscopic fluctuations instead of microscopic thermal fluctuations (FT)

• This will also work in experiments
Suspensions of Hard Spheres
Jarzynski and Crooks Relation

in the NPT ensemble

\[ \langle \exp(-\beta W) \rangle = \exp(-\beta \Delta G) \]

G: Gibbs Free Energy

with the underlying symmetry

\[ P(W) = P^\dagger(-W) \exp(\beta(W-\Delta G)) \]
Jarzynski and Crooks Relation

in the NPT ensemble

\[ \langle \exp(-\beta W) \rangle = \exp(-\beta \Delta G) \]

G: Gibbs Free Energy

with the underlying symmetry

\[ P(W) = P^\dagger(-W) \exp(\beta(W-\Delta G)) \]
\[ W = \int_0^{\tau} \, \text{d}t \, P' \, V(t) \]

\[ \langle \exp(-\beta W) \rangle = \exp(-\beta \Delta G) \]
Work Distribution
Compression in the fluid phase

Numerical study:
N=540 spheres,
initial pressure
P=8, pressure
increase $\Delta P=3$

distributions for
different tau
Work Distribution
Compression in the fluid phase

Numerical study: N=540 spheres, initial pressure P=8, pressure increase ΔP=3

distributions for different tau
Work Distribution
Compression in the fluid phase

Numerical study: N=540 spheres, initial pressure P=8, pressure increase ΔP=3
distributions for different tau

ΔG

Wednesday, March 13, 13
Crystallization Event - Compressing into the solid phase

Pressure, $P$

Volume fraction, $\phi$

Freezing 0.494  Melting 0.545  RCP 0.640 (?)  FCC 0.740

$P_{\text{fin}}$

$P_{\text{ini}}$
Jump in the Volume

Volume as a function of time
\[ \Delta P=15, P_{ini}=8, t=200000 \]

Volume as a function of time
\[ \Delta P=15, P_{ini}=8, t=1000000 \]
Appearance of crystal structures

Number of solid particles as a function of time
\( \Delta P = 15, P_{ini} = 8, t = 200000 \)

Number of solid particles as a function of time
\( \Delta P = 15, P_{ini} = 8, t = 1000000 \)
Work distribution

Slow process, $\tau=500000$ MCsteps, $P_0=8$; $\Delta P=15$
Work distribution

Slow process, $\tau=500000$ MC steps, $P_0=8$; $\Delta P=15$
Work distribution

Slow process, $\tau=500000$ MCsteps, $P_0=8$; $\Delta P=15$
Work distribution

Slow process, $\tau=500000$ MCsteps, $P_0=8$; $\Delta P=15$
Work distribution

Slow process, $\tau = 500000$ MCsteps, $P_0 = 8$; $\Delta P = 15$
Where am I in this project?

- simulations are running - unbiased.
- rare event sampling not setup yet - needs to be done.
- delta G needs to be obtained to compare to results via Jarzynski relation. forward and reversed process separately.
- no long ellipsoids considered yet ... (consider fluid nematic transition )
Modeling of the process

• Input of all the equilibrium properties at fixed pressure
• Input of the nucleation rates
• obtain work distributions → Compare to MC simulation
• supervision of Master student (next three months)
Where am I in this project?

- Again, I need to calculate the free energy difference to compare to simulation results.
- check the relation \( \Delta G = <W> - <W_{diss}^2>/k_b T \) (Gaussian approximation)
- reversed process not realized yet.
- i need to obtain melting rates...
Other ongoing projects

• Compression in centrifuge > Work distribution measurement (project with INM Saarbruecken and T.Platini Coventry University) (open questions: Thermostat EDMD algorithm, determine local pressure inside the suspension.)

• Structure factor measurements for ellipsoid suspensions (Martschenko Lundt University) (open questions: too many parameters to play with)

• Charged ellipsoids + Derjaguin approximation (project with Tanja, Martin Oettel)

• Crystallization in system of hard spheres including random pinning. Frustration causes changes in energy barriers.
Further Goals of the Project

• organize workshop in Luxembourg, fix the list of speakers
• visit schools and organize stand at the researchers night for students.
• Lecturing.
• habilitation at the end of the three years.
• think about plans for after the project (Spring 2016).